KOCH

The Action of Hydrazine on Ethyl Dihydroxymalonate

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THE ACTION OF HYDRAZINE
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BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Alfred Richard Koch.

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

in Chemical Engineering.

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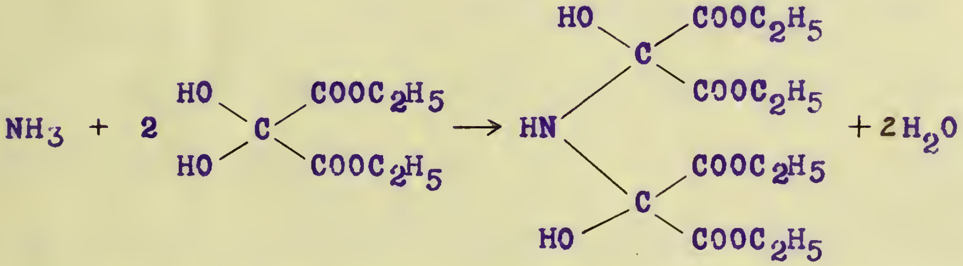
ACTION OF HYDRAZINE ON ETHYL DIHYDROXYMALONATE

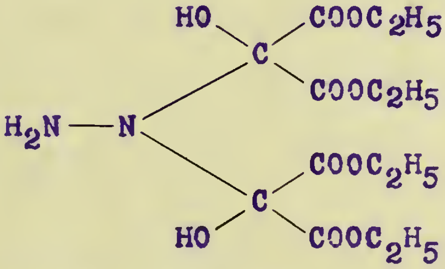
by

Alfred Richard Koch.

In his work on mesoxalic esters, R. S. Curtiss[1] obtained ethyl dihydroxy-iminodimalonate by the action of dry ammonia on ethyl mesoxalate in cold dry benzene solution.



This and other considerations, led to the question whether hydrazine would act in the same way and give a compound of the formula



in which the imine-hydrogen atom of the dihydroxy-iminodimalonate would be replaced by an NH_2 group.

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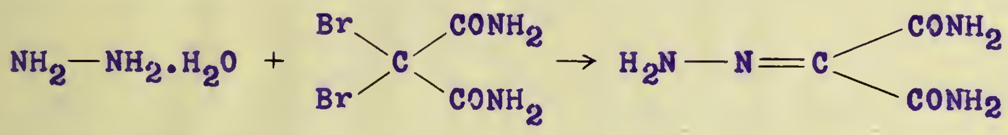
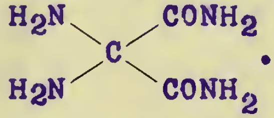
[1] Amer. Chem. Jour. 35, 356.

Ruhemann and Orton[1] have made the hydrazone of mesoxalamide (hydrazinomesoxalamide) by treating dibrommalonamide with hydrazine hydrate,



By treating dibrommalonamide with ammonia they obtained diaminomalonamide,



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In these reactions the hydrazine and ammonia do not act in an analagous manner, only one molecule of hydrazine, whereas two molecules of ammonia take part in the reaction with one molecule of dibrommalonamide.

When hydrazine acts on malonic ester, even cold, malonylhydrazide, $H_2C(CO.NH.NH_2)_2$, is formed just as, according to the general rule, other esters, formic[2], acetic[3], oxalic[4], and succinic form the corresponding hydrazides.

As will be shown further on, when hydrazine hydrate acts on ethyl dihydroxymalonate the ester is not saponified but an addition reaction takes place.

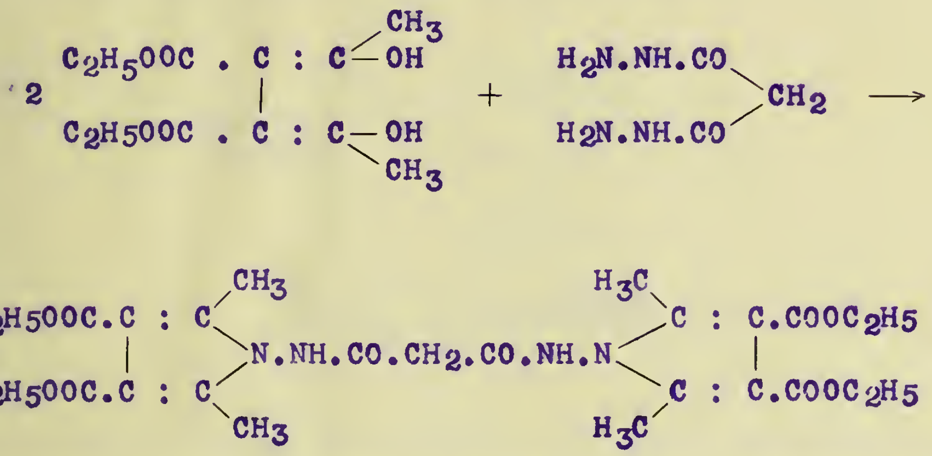
[1] Journ. Chem. Soc. 1, 1002.

[2] Schöfer, Schwan, Journ. f. pr. Chem. (2) 51, 180.

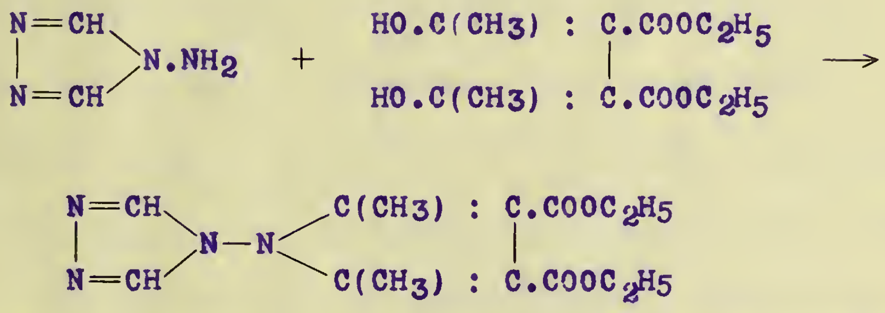
[3] Ibid, (2) 51, 185, and Curtius and Hofmann, Jr. pr. Ch. (2) 53, 524.

[4] Schöfer, Schwan, Jr. pr. Ch. (2) 51, 194.

Bülow and Weidlich[1] studied the reaction between malonylhydrazide, which may be considered as a derivative of hydrazine, and diacetsuccinic acid ester



A similar reaction, between a substituted hydrazine, andhydroxyl groups, takes place when "dihydrotetrazine" acts on diacetsuccinic ester,[2]



This reaction between the amine and hydroxyl groups is somewhat analogous to that obtained with hydrazin and ethyl

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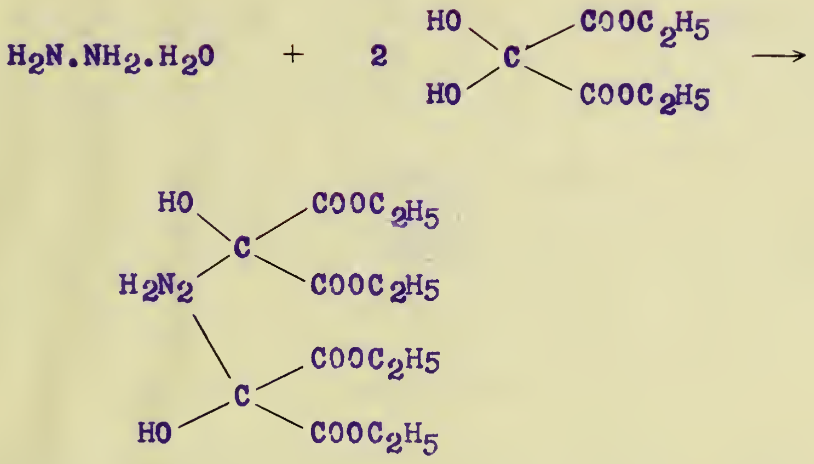
[1] Ber. 39, 3372-3377.

[2] Carl Bülow, Ber. 39, 2618-2622.

dihydroxymalonate,



The Action of Hydrazine Hydrate on Ethyl Dihydroxymalonate.

The best product was obtained by adding 7.5 grams (2 mols.) of pure ethyl dihydroxymalonate (m. p. 57°), prepared as already described,[1] to 10 c. c. (1 mol.) of an approximately 6.5 per cent hydrazine solution. Practically all of the ester was added at once to the hydrazine solution, in an Erlenmeyer flask, and then allowed to stand for three minutes. Before all of the ester dissolved the liquid became turbid and a few seconds later globules of a white oil collected and dropped to the bottom of the flask. The odor of hydrazine disappeared shortly after mixing, but at the time of the separation of oil, the air above the liquid was slightly alkaline. The oil

[1] Curtiss, Amer. Chem. Journ. 35, 477.

remainded colorless while the color of the supernatant aqueous liquid became pale yellow. When this color appeared the reaction was complete and the flask was then placed in a freezing mixture for a few minutes. Soon the separated oil became doughy and began to crystallize in the form of beautiful white radiating clusters on the surface of the oil, and on the sides and bottom of the flask. These crystals melt at -4 to -5 degrees and yield again a white doughy mass, which becomes a clear oil at ordinary temperatures. Simultaneously with the melting of these crystals, other crystals had formed up on the neck of the flask, at room temperature. These latter, placed in the oily mass, caused it to become turbid and to change to a crystalline body melting at 57° - 58°. The contents of the flask were then cooled for 20-25 minutes, filtered with a pump, and washed with ice water three times. The crude product weighed 5.9 grams. The mother liquor was extracted with ether and one gram more of the same white crystalline body was thus obtained.

If these conditions are not strictly adhered to an apparent polymerization takes place, indicated initially by a red coloration in the solution, and the whole product goes to a thick red gum, or resinous mass, which is incapable of

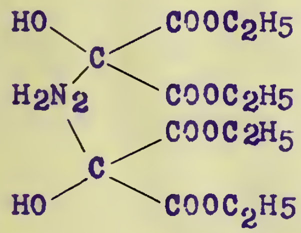
further purification. The first experiments were carried out with alcoholic solutions of ethyl mesoxalate, (both the oxo- and dihydroxy- bodies), and hydrazine hydrate, and invariably led to a red gummy mass if allowed to stand very long, especially if at ordinary room temperatures.

The crude product obtained above was recrystallized from a solution of equal parts of ligroin and benzene and dried in a vacuum des~~s~~iccator. An analysis of this substance, of melting point 58°, gave the following results:--

I. 0.2003 gram substance gave 0.3208 gram CO_2 and 0.1084 gram H_2O.

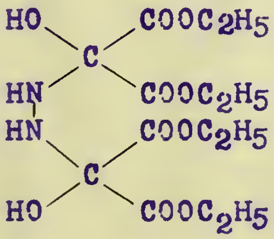
II. 0.1921 gram substance gave 12.' c. c. N at 20° and 760 mm.

III. 0.2524 gram substance gave 17.75 c. c. N at 21° and 758.75 mm.

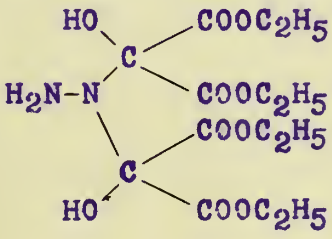
	Calculated for	Found		
		I.	II.	III.
C	44.17%	43.63%	-----	-----
H	6.36	6.04	-----	-----
N	7.38	----	7.62%	7.98%

The results of the analyses show that the substance has the composition corresponding to the above formula.

Properties. It is obtained as above in white crystals, apparently rhombohedral, which melt at 58°. It is easily soluble in hot water, ether, benzene, chloroform, ethyl alcohol, methyl alcohol, acetic ether, and hot carbon bisulphide. It is fairly soluble in carbon tetrachloride, and in cold water. It dissolves with difficulty in cold carbon bisulphide. In cold ligroin, it is nearly insoluble. The pure substance has a bitter taste like quinine. On standing two or three days in a vacuum dessicator with sulphuric acid, it is changed to a thick colorless oil, apparently dehydrated. No apparent change takes place in the open air even after standing a long time (two months). When heated in a test tube, it melts and gives off a vapor which condenses on the upper portion of the tube as a colorless liquid, like water, and leaves a residual thick yellow or green oil. There are two possible structural formulas for a substance of the composition indicated by the above analysis,



and



To answer the question as to which of the above formulas is the correct one, the following preliminary tests have been made.

a) When an aqueous solution of the substance with silver nitrate is allowed to stand ten minutes, a colorless gas is given off and metallic silver is deposited. The same reducing effect is obtained when platinic chloride is used, when beautiful shining plates of metallic platinum are slowly deposited.

b) When fused in a test tube with soda lime or aqueous potassium hydroxide, an ammonia-like odor is given off (hydrazin?). Solutions of the substance with potassium hydroxide or potassium carbonate cause a yellow coloration, and finally the solution changes to a red gum.

c) When oxidized with nitric acid a large evolution of gas results.

d) Concentrated hydrochloric acid gives a white oil as the chief product, together with some white crystals, soluble in water, and containing chlorine. Dry hydrochloric acid passed into a dry ethereal solution of the substance yields a yellow oil as main product and some white crystals, which are soluble in water.

e) When concentrated sulphuric acid is added to a saturated aqueous solution of the substance, a white oil and a white crystalline substance, soluble in excess of acid but insoluble in ether, are formed. Concentrated sulphuric acid dissolves the dry substance and on diluting with water a yellow oil, together with white crystals are formed.

f) Action of ethyl nitrite on this substance: One cubic centimeter of distilled water was added to 0.38 gram (1 mol.) of the substance and cooled in a freezing mixture. One minute later 0.075 gram (1 mol.) of cold ethyl nitrite was added and after two more minutes 1 c.c. of cold normal sulphuric acid was added, a very little at a time. Immediately on adding the acid a gas is evolved and an oil begins to form. After freezing the solution and again melting it, a white crystalline substance formed, which was soluble in ether. After extracting thoroughly with ether and evaporating off theether, the product remaining was shown, by numerous tests, to be ethyl dihydroxymalonate. In the aqueous liquid a crystalline substance which decomposes at 253° was found. The same experiment was carried out in the absence of water by substituting 0.7 c. c. absolute alcohol for the 1 c. c. of water. The other conditions were exactly the same as in the previous experiment. Two white

crystalline substances were the result. One of them, soluble in ether, was ethyl dihydroxymalonate; and the other, insoluble in ether but soluble in water, decomposed at 253°, as did the product of the previous experiment. A dry ethereal solution of one molecule of the substance together with one molecule of amyl nitrite, after standing at ordinary temperatures for several days, gives an oil which decomposes when distilled. As Liebermann's test gives no color reaction with this oil, apparently no nitrosamines are formed. In these attempts at diazotizing, the nitrogen is split off and the ketone ester regenerated.

g) When phosphorus pentoxide is allowed to act on this substance, either directly or in a cold ethereal solution, the product is a pale yellow oil. An apparent dehydration takes place.

h) 2.54 grams (1 mol.) of the substance were treated with 1.88 grams (2 mols.) of benzoyl chloride at a temperature of 40°-50°. A small quantity of a white crystalline substance immediately forms which is insoluble in ether and melts at about 230°. On heating the substance with benzoyl chloride for three hours on the water bath and then allowing it to cool, a yellow crystalline substance is formed.

i) When heated for two hours on the water bath with acetyl chloride (3 mols.), extracting with ether and evaporating off the solvent, a product remains as a clear yellowish green oil.

j) It gives with acetic anhydride on standing two days in a des~~s~~iccator a clear colorless syrup.

k) 1.9 grams (1 mol.) of the hydrazine derivative were melted and then 0.53 gram of benzaldehyde was added and the temperature kept at about 60°. After standing at this temperature for 40 minutes, a thick amber-colored oil had formed and drops of water condensed on the sides of the flask. Small pieces of calcium chloride were added which caused the oil to clear. Sixteen hours later the oil was extracted with dry ether and the ether evaporated off at 60°. A clear, thick, amber-colored syrup remained. This action with benzaldehyde shows that hydrogen atoms are connected directly to the nitrogen atoms.

l) Phosphorus pentachloride acting on the substance gives off volumes of gaseous hydrochloric acid. This proves the presence of hydroxyl groups.

In the early stages of this work the first experiments on the action of hydrazine hydrate on ethyl mesoxalate were carried out in alcoholic solutions. The product always became gummy and difficult to purify. After making many experiments, varying all the conditions, such as temperature, concentration, order and rapidity of mixing, etc., the purest product and best yield was finally obtained as follows:-- 0.17 gram (1 mol.) of ethyl dihydroxymalonate was dissolved in 1.5 c. c. of alcohol. This was slowly poured down the side of a test tube into 1.9 c. c. of alcohol containing 0.4 c. c. (2 mols.) of a 22% hydrazine hydrate solution. Care must be taken not to mix the two solutions, else gummy products form. As soon as the two liquids came into contact a white turbidity began to form at their juncture. The tube was corked and allowed to stand at a temperature of about 10°. After 40 minutes, needle-like crystals had formed on the lower side of the upper liquid layer and were falling to the bottom of the tube. The next day the lower half of the liquid was filled with beautiful clusters of needles. The mother liquor was a clear pale yellow. 0.11 gram of yellowish white crystals was filtered off and washed with ether. Attempts to recrystalline the substance decomposed it. Analyses were made of the crude substance with the following results:--

I. 0.2060 gram substance gave 21.5 c. c. N at 23° and 755.25 mm.

II. 0.1940 gram substance gave 0.1490 gram CO_2 and 0.0990 gram H_2O.

III. 0.1290 gram substance gave 0.0972 gram CO_2 and 0.0654 gram H_2O.

Found.

	I.	II.	III.
C	-----	20.92%	20.54%
H	-----	5.67	5.66
N	12.01	----	----

The empirical formula corresponding to the above results is very nearly $C_4H_{13}N_2O_9$.

The results of the tests on this substance are as follows:-- It decomposes at 125°-130°, evolving a gas and leaving a yellow body, which gives off a gas and melts to a red liquid at 170°. It is easily soluble in warm water, and in potassium hydroxide solution which then becomes yellow. It is fairly soluble in cold water. It dissolves with difficulty in ether, methyl alcohol, hot absolute alcohol, acetone, benzene, carbon bisulphide, and 24% acetic acid. It is insoluble in chloroform, carbon tetrachloride, ligroin, and nitrobenzene. Its aqueous

solution when boiled turns red, the presence of alcohol hastens this decomposition.

Glacial acetic acid added to its cold, yellow, aqueous solution gives a heavy white flocculent precipitate. The latter dissolves in excess of the hot acid to a yellow solution, from which the white substance again precipitates on cooling. This white product from glacial acetic acid is insoluble in ether, alcohol, acetic ether, and carbon tetrachloride. It is almost insoluble in absolute alcohol, methyl alcohol, benzene, acetone, ligroin, chloroform, and cold water. It is slightly soluble in hot water, and hot acetic acid. The hot acetic acid solution is golden yellow, aqueous potassium hydroxide changes it to blood red, and this is again changed to yellow by hydrochloric acid. It decomposes at about 220°. When heated in a test tube, as soon as ~~a certain~~ this temperature is reached, it suddenly decomposes, giving off a vapor with an odor of ammonia or hydrazine, and leaves a large charred residue. The gas given off on strong heating forms with hydrochloric acid a white substance which immediately gives a silver mirror, on heating in ammoniacal solution with silver nitrate, and is probably a hydrazine salt.

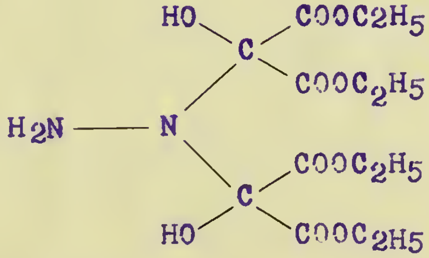
This substance formed from ethyl dihydroxymalonate and

hydrazine hydrate and decomposing at 125-130°, when heated with benzaldehyde, gives off a gas with water vapor. After cooling and washing with benzene the product is a bright yellow solid which decomposes at 163°. This substance reacts with hydrochloric acid forming yellow needles.

The main conclusions to be drawn from this work are as follows:--

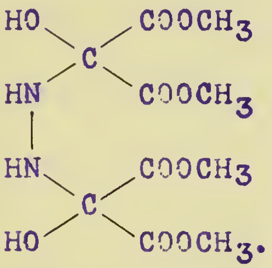
1. Aqueous hydrazine solutions give different products with ethyl mesoxalate, depending upon the conditions of temperature, concentration, solvents, and manner and rapidity of mixing.

2. The chief product here studied is unstable, readily changing in dry air and under most reagents, especially those which have a dehydrating action. It is probably ethyl hydrazinoditartronate,



in which only one nitrogen of the hydrazine molecule is attached to the two radicals of ethyl tartronate, forming an unsymmetrical hydrazine derivative.

This formula is tentatively given and is based on the above, as well as additional evidence recently obtained, and by a comparison of its properties with those of the supposed isomeric form of the methyl ester[1],



This substance is also being studied. It behaves in all its reactions quite differently from the product described in this paper, which fact is suggestive of this difference in structure.

3. Operating in alcoholic solutions the tendency is to form resinous polymerization products. Under certain exact conditions a crystalline substance is formed, markedly different from the above ethyl hydrazinoditartronate. The constitution of both is being further studied in this laboratory.

Laboratory of Organic Chemistry,
May 31, 1907.

Finis

Alfred Richard Koch
in conjunction with
Richard S. Curtiss.

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[1] See Thesis of P. T. Tarnoski, page 12. This Laboratory, June, 1907.